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PROCESS FOR THE PRODUCTION OF A PRESSED INSENSITIVE EXPLOSIVE MIXTURE

DESCRIPTION Related Applications

This application is a continuation-in-part (CIP) application of U.S. application Serial No. 10/170,974, filed June 13, 2002.

Field of the Invention

The present invention relates in general to insensitive, yet fully energetic high explosive molding powders using sonochemically aminated 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) as an energetic binder, i.e., adhesive. The sonochemically aminated TATB is used at a relatively low weight % level (less than 15% by weight) in comparison to conventional crystalline TATB.

Background of the Invention

Crystalline TATB is a very insensitive secondary high explosive that is characterized by a reactively low energy output, in terms of metal liner acceleration, and a very high price per kg, which is caused by subjecting the crystals to multiple intense neutralization cleansings. To improve metal liner acceleration of crystalline TATB, a relatively low percentage of approximately 20 to 40 weight % of RDX (known variously as cyclonite, cyclotrimethylenetrinitramine and 1,3,5-trinitro-1,3,5-triazacyclooctane) or HMX (known variously as cyclotetramethylenetetranitramine, and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane) including different "inert" binders were added in numerous insensitive, high explosive mixtures in order to remain within the "less sensitive" requirements of STANAG 4170. This is disclosed, for example, in U.S. Patent No. 6,485,587 B1 for an explosive mixture known as PBXN 7 which contains 66.5% weight TATB, 29.5% weight RDX and a relatively high content, i.e., 5% weight, of the inert

binder system HYTEMP(a polyacrylic elastomer)/DOA (di-(2-ethylhexyl)-adipate), thus the 100% theoretical maximum density (t.m.d.) is only 1.83 g/cm².

Driven by the high price of conventionally produced crystalline TATB, there is ongoing research to find more cost effective methods of producing insensitive high explosive mixtures. For example, Chemical Abstracts 129:138150n entitled "Synthesis and initiation spot-size testing of sonochemically aminated TATB", Lee, Kennedy and Stein, *Int. Annu. Conf. ICT*. 1998, 29th (Energetic Materials), 177.1-177.14 discloses a relatively simply synthesis method which avoids expensive washings/waste control. Specifically, TATB is synthesized from 1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB) by amination with NH₄OH under the influence of ultrasonic irradiation. Moreover, there is a suggestion therein "of a higher initiation sensitivity" for the disclosed sonochemically aminated TATB over existing TATB as disclosed in U.S. Patent No. 6,547,899 B2.

Intending the use of sonochemically aminated TATB as a replacement for even less metal liner acceleration capability HNS IV, the applicants of the present application reproduced the method described in Chemical Abstracts 129:124495a, entitled "Characterization of sonochemically-aminated 1,3,5-triamino-2,4,6-trinitrobenzene" Bremser, et al., *Int. Annu. Conf. ICT* 1998, 29th (Energetic Materials), 13.1-12.13 without the use of the pressurized reactor described therein. The material reproduced from the Bremser, et al. method did not experience a significant increase of sensitivity at pellet densities from 1.65 g/cm² to 1.92 g/cm².

In another experiment, the applicants of the present application modified the procedure described by Bremser, et al., again without the use of a pressurized reactor, to obtain TATB crystals having approximately 1 μm median particle diameter. These crystals also did not exhibit any increase of sensitivity as was described by Bremser, et al. During BICT-Small Scale Gap Tests, the insensitivity of this prior art sonochemically aminated TATB sample still remained far beyond the desired shockwave level of 46 kbar.

Summary of the Invention

Having analyzed the polarities and molecular properties of high explosives such as, for example, RDX and HMX, in relation to TATB, such properties offered to the applicants of the present invention high polarity bonding between the high energetic explosives and TATB thus avoiding, with a high probability, the addition of inert binders. Moreover, this data suggested the possibility of employing a relatively low % weight of sonochemically aminated TATB because of its inherent coating capability, especially when it is mixed with HMX. Hence, the applicants have determined that a low % weight of sonochemically aminated TATB of less than 15% can be used to reduce the sensitivity significantly of a HMX mixture below the threshold of the "less sensitive" requirements.

Quicklook tests by the applicants confirmed the above analyses, especially for HMX coarse grains and TATB having a mean particle diameter of about 6 to about 8 μm , showed an excellent adhesive behavior during dry or wet mixing. Further analysis of pressability and shock sensitivity of small pellets using different HMX classes of quality B following the rules of harmonic contents of the different grain size distributions for maximum crystal density packages led to pellet densities of 1.92 g/cm^3 which meets shock insensitivity criteria's already at a 5% weight content and the status "less sensitive" of STANAG 4170 between 10% and 15% weight content of this type of TATB only, without presence of any binder.

Using 1 μm sonochemically aminated TATB in HMX mixtures led to a crack at the half length of the pellet thus increasing the shock sensitivity level out of the insensitive regime, however the addition of less than 1% weight binder HYTEMP led to no more cracks. The goal to achieve 100% energetic pellets from this very fine grain TATB mixed with HMX crystals failed; the coating however was able to withstand uncoating tests with solvents, such as acetone, alcohol, methanol, and ethyl ester.

Resulting from this experience, the applicants have developed an "in-situ" method for coating HMX crystals with TATB during sonochemical amination of TCTNB (Trichloro-Trinitro-Benzene) in ammonium hydroxide solution achieving uniform coating of the HMX crystals with 5% weight and 1% weight TATB. The mechanism indicates that even thinner coatings resistant to solvents, especially on HMX, can be achieved down to a few molecular layers filling up crystal surface microholes and microcracks of today's crystals qualities or even on tomorrow's more perfect crystals thus densibilizing high explosive crystals to be used in insensitive molding powders and castable mixtures. Depending on the possibility of interaction of the high explosive crystals, in terms of space (distance) and time, with the ultrasonic waves, in addition a milling treatment of especially HMX and Cl 20, can be conducted leading to crystals having mean diameters down to 1 μm .

To achieve the foregoing high explosive, high energetic insensitive molding powder and other objects of the present invention and in accordance with other purposes described herein sonochemically aminated TATB made through the modified process described above is used as an energetic binder for high energetic explosives achieving sufficient insensitivity of molding powders with a 5-15% weight content.

The use of sonochemically aminated TATB as a binder, i.e., as an adhesive, provides relatively high pellet densities without any additional binder as compared to conventional TATB mixtures to HMX/TATB having pellet densities of up to 1.92 g/cm². Sensitivity to mechanical stress cracks of minor nonharmonic grain size distributions can be eliminated in the present invention by the addition of less than 1 % weight of a binder, preferably HYTEMP, to the explosive mixture of TATB and secondary explosive crystals.

Stated in broad terms, the present invention provides a process for preparing pressed insensitive explosive mixtures that includes a step of depositing sonochemically produced TATB onto secondary explosive crystals. In some embodiments, the sonochemically produced TATB employed in the present invention has a small particle

diameter of less 1 μm and is synthesized from 1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB) by amination with NH_4OH under the influence of ultrasonic irradiation. The process of present invention results in a pressed insensitive explosive mixture that includes secondary explosive crystals that are bounded together with sonochemically produced TATB.

Having modified the above mentioned process in a second step an "in-situ" or direct desensibilization coating of high explosive crystals can be achieved for further use either in molding powders or castable insensitive high energetic high explosive mixtures.

Detailed Description of the Invention

As stated above, the present invention provides a process for producing pressed insensitive explosive mixtures in which secondary explosive crystals are bounded together with sonochemically produced TATB. An additional binder such as, for example, HYTEMP, phthalates such as DOA, calcium stearate, fumed silica or other like conventional binders may also be present in the pressed insensitive explosive mixture of the present invention. HYTEMP is a polyacrylic elastomer sold by Zeon Chemical L.P., Bells Lane-Louisville, Kentucky 40211. Combinations, i.e., binding systems, of the aforementioned additional binders are also contemplated in the present invention. When used, the additional binder is present in an amount from about 0.1 to about 3% by weight. The additional binder provides for more control of the properties of pressed bodies.

Examples of secondary explosive crystals that can be used in the present invention include, but are not limited to: RDX, HMX, CL-20 (2,4,6,8,10,12-hexanitro-hexaaisowurtzitane; HNIW), PETN (pentaerythritol tetranitrate) and other like explosive crystals. Combinations of the secondary explosive crystals are also contemplated in the present invention. Preferred secondary explosive crystals are HMX crystals. The grain size and crystal mean diameter of the secondary explosive crystals employed in the present invention may vary.

The amount of secondary explosive crystals included TATB present in the inventive pressed insensitive explosive mixture is from about 97 to about 100 %, by weight, with an amount from about 99 to about 100 % being more preferred.

The binder of the inventive pressed insensitive explosive mixture is sonochemically aminated TATB. The sonochemically produced TATB employed in the present invention has a mean particle diameter of 6 to 8 μm , and less than 1 μm depending on intended application.

The sonochemically produced TATB is synthesized from 1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB) by amination with NH_4OH under the influence of ultrasonic irradiation using procedures well known in the art.

Specifically, the sonochemical synthesis of TATB involves a two-phase reaction wherein a solution of TCTNB (trichlorotrinitrobenzene) in toluene is reacted with an ammonia solution that is immiscible with the solution of TCTNB. The activation energy needed in the aforementioned reaction is supplied by using a strong ultrasonic source. The ultrasonic source also provides for a significant increase in the phase interfaces at which the chemical reaction takes place.

In some embodiments, the sonochemical TATB can be produced by dropping a TCTNB solution into a saturated solution of ammonia to produce refined TATB crystals. This method provides a higher degree of wetting in regard to explosive crystals. This method is also a prerequisite to form automatic production of the explosive mixture of the present invention.

The very fine TATB which is produced upon the reaction taking place can be filtered off, washed and dried, and can then be used as a binder for secondary explosive crystals.

The pressed insensitive explosive mixture of the present invention contains from about 3 to about 15 % by weight of sonochemically TATB, with an amount from about 5 to about 12 % by weight being more preferred.

In an alternative mode of production, the following can be employed in the present invention: Using ultrasound, a suspension comprising the respective secondary explosive (in a, as delivered, moistened condition), that is to say secondary explosive crystals in an excess aqueous (about 30%) ammonia solution is produced, and an amount of TCTNB, calculated in accordance with a reaction conversion effect, dissolved in toluene is added by dropwise.

The resultant very fine TATB produced by this alternative method can now be deposited directly in-situ on the suspended secondary explosive crystals. This results in a TATB coating on the secondary explosive crystals. That is, the TATB fills in the pores of the rough secondary explosive crystals providing a product that is relatively smooth.

It was determined by laser diffraction measurements that, by virtue of the foregoing dropping process, in comparison with the conventional dropping process, it is possible to achieve a further reduction in the mean particle diameter of the TATB particles, which in turn further improves the adsorptive capability.

The adsorption procedure is also enormously promoted by the formation of strong hydrogen bonds between the nitro groups of the secondary explosive crystals and the amino groups of the TATB.

After the addition of the sonochemically produced TATB to the secondary explosive crystals, the resultant product is recovered by filtering, washing and drying in vacuum.

The resultant produced, i.e., TATB bound explosive crystals or TATB coated explosive crystals, can be passed directly for further processing.

As indicated above, the insensitive explosive mixture of the present invention has TATB deposited directly on the secondary explosive crystals which mixture can be used for the crack-free production of pressed explosive bodies. The pressed explosive bodies may contain small proportions of additional binders that can be added during the production of the insensitive explosive mixture.

The following examples are provided to illustrate the scope of the present invention, as well as some advantages that can be obtained therefrom.

Example 1

In this example, a HMX/TATB molding powder comprised of 70% weight. coarse grain HMX type B or A with crystal mean diameter of 45 μm and 30% weight fine grain crystals having a crystal mean diameter of 6-8 μm was provided. This fine grain is comprised of the required content of sonochemically aminated TATB 6-8 μm between 5 to 15% weight and the remaining portion to 30% weight is HMX having same crystal mean diameter. Mixing can be done with dry crystals at ambient temperature in any mixer, preferably however is the use of crystals that are wetted with a solvent such as ethyl acetate, and/or methyl isobutyl ketone or other solvents, and then homogenized for 30 min at medium revolution speeds of the mixer and then heated and/or vacuum assisted drying of the mixture at moderate revolution speed foreseen for the used mixer. The dried mix is ready for vacuum pressing of pellets at vacuum smaller than 1 mbar. Because of the same density of HMX and TATB and their molecular polarity adhesion, no sedimentation of one of the ingredients occurred during storage. This molding powder is a type preferably for use in small ordnances like insensitive boosters.

Example 2

HMX/TATB molding powder preferably comprised of 64% HMX type B or A grain class C, no crystal larger than 500 μm , second portion of 24% weight HMX having crystal mean diameter of approximately 45 μm and 12% sonochemically aminated TATB 6-8 μm . The mixer kettle is first loaded with a solvent mixture of 50% weight acetone and 50% weight ethyl acetate or a (mono)-methyl ketone with 10% to 30% weight of the explosive components. The high explosive crystals are filled into the kettle without any order. The procedure for homogenizing and drying is as described in example 1 however a high shear mixer type should not be used. This molding powder type is preferably for use in larger caliber boosters and directed energy warheads, e.g., shaped charges of EFP chargers one in other maximum performance warheads. Depending on the desired insensitivity of the warhead the TATB content may be varied.

Because of leaving in this case the rules of harmonic grains size distributions and scattering of high explosive crystal batches due to production process tolerance there is an increased probability of desensibilizing microcracks in the pellet. Adjustments can be made by small percentage changes of coarse and fine grain HMX crystals towards tetramodality (64:24:9:3) and substitution of 3% of the TATB 6 to 8 μm with by TATB mean diameter 1 μm , at other reductions the 6 to 8 μm TATB may be substituted by the same percentage of HMX 6 to 8 μm . Larger deviations from harmonic grain size distributions, e.g., a TATB 6 to 8 content of 15% weight require addition of a binder, preferably HYTEMP, up to 1% weight, of the high explosive crystal mass. This HYTEMP shall be solved and added to the mixer as a low viscosity lacquer, at 1% HYTEMP there is a remarkable loss of the achievable t.m.d.

Example 3

Coating of HMX crystals with TATB. The required amount of dissolved TCTNB is added as quickly as possible to the reactor. Depending on the reactor size a few minutes, approximately 10% of the given number in U.S. Patent No. 6,547,899 D2 the sonochemical amination is conducted. Immediately after this treatment, the predetermined amount of HMX crystals are added and an immediate adhesion of TATB will occur. This slurry needs to be filtered and after sequential washing with water and toluene the crystal mass is dried in an oven and then ready for further use in insensitive molding powder or castable formulations.

Example 4

Very coarse grain HMX is added to the sono-reactor at the beginning of the standard sonochemical amination process described in U.S. Patent No. 6,547,899 D2. Depending on the concentration of the HMX in the slurry, the HMX will be milled by time by the strong sonowaves to bimodal grain distribution or to crystal sizes of 1 μm and at the same time coated with the nascent TATB at a predetermined HMX/TATB ratio. The following procedures are the same as described in example 3 as well as the further use if these coated crystals. Described method allows to have available multimode grain size distribution at the time required having only e.g. HMX class C crystals in stock or simply to refine undesired HMX crystals larger than 500 μm .

While the present invention has been particularly shown and described with respect to preferred embodiments, it will be understood by those skilled in the art that the foregoing and other changes in forms and details may be made without departing from the spirit and scope of the present invention. It is therefore intended that the present invention not be limited to the exact forms and details described and illustrates, but fall within the scope of the appended claims.